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Syn-gas-based mono ethylene glycol synthesis in Pujing Chemical

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Abstract Mono ethylene glycol (MEG) is a kind of important fundamental chemical, mainly used in polyester synthesis. Traditional MEG production is based on petroleum resources. This study reports about a new kind of MEG technology to synthesize CO and hydrogen, developed by Pujing Chemical. Laboratorial researches were performed well by developing both carbonylation catalyst and hydrogenation catalyst. Later, a 300 t/a hydrogenation pilot plant was employed to verify the hydrogenation catalyst, and another 1000 t/a pilot plant was set up to validate the whole flow process, catalysts and purification technology in Anhui Province, China.

Keywords Mono ethylene glycol · Carbonylation · Hydrogenation · Pilot plant

Introduction

Mono ethylene glycol (MEG) is mainly used for polyester, solvent and antifreeze in engine, as well as producing resin, plasticizer, cosmetic and dynamite. In 2011, MEG is projected to be consumed at a huge amount of around 20,000 kt/a world wide and about 8,000 kt/a in China. Nowadays, traditional MEG production is based on petrochemical route, originating from petro-ethylene via oxidation followed by hydration process [1]. However, the depleting petro-resources put high pressure on the countries and/or districts lack of petroleum to keep developing, such as China. Therefore, developing a new process from non-petroleum resource (i.e. coal-based or natural-gas-based syn-gas) to be an alternative for petroleum-based process will become highly attractive.

Under such a circumstance, Pujing Chemical corporate with East China University of Science & Technology and developed a kind of technology [2–5] to prepare MEG from CO and H_2, which consists of methyl nitrite (MN) regeneration, dimethyl oxalate (DMO) production, MEG synthesis and MEG purification. The flowchart is shown as Fig. 1.

In the whole process, MN, NO and methanol (ME) recycle and do not lose theoretically. The related reactions are presented as follows:

$$\text{MN Regeneration}: 2NO + 0.5O_2 + 2CH_3OH = 2CH_3ONO(MN) + H_2O$$

$$\text{DMO Synthesis}: 2CH_3ONO + 2CO = CH_3OCOCOOCH_3(DMO) + 2NO$$

$$\text{MEG Production}: CH_3OCOCOOCH_3 + 4H_2 = CH_2OHCH_2OH(MEG) + 2CH_3OH$$

$$\text{Total}: 2CO + 0.5O_2 + 4H_2 = CH_2OHCH_2OH(MEG) + H_2O$$

The technology of CO coupling reaction to produce dimethyl carbonate (DMC) and/or DMO via intermediate of alkyl nitrite was initially developed by Ube Corporation [6], however, Pujing reduced the cost of carbonylation catalyst to a large extent by further investigation of the coupling mechanism [7, 8] and, importantly developed a kind of environmental-friendly hydrogenation catalyst, Cu–Si catalyst [9], rather than Cu–Cr catalyst.

In the following text, we will report Pujing's MEG technology from laboratorial experimental to pilot plant.

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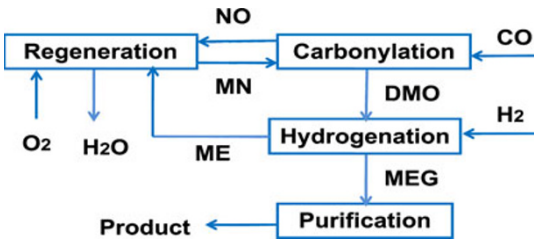

Fig. 1 MEG production from CO and H_2

Laboratorial experimental

MN regeneration can take place without catalyst, while both carbonylation and hydrogenation have to depend on catalysts. In laboratory, we mainly introduce two kinds of catalysts.

Carbonylation process

Carbonylation reaction of CO and MN takes place over Pd catalyst. Pujing Chemical employed proprietary technology to prepare egg-shell Pd/α-Al_2O_3 catalyst, and studied the influence of precursors' pH value on the depth of egg shell and investigated the activity and selectivity during the reaction for serial C catalysts.

As shown in Fig. 2, low pH value of precursor produces higher depth of the shell, while basic solution could decrease the thickness. The table illustrated that except DMO, DMC is the main by-product with some ME and MF (methyl formate). The catalyst prepared under acid liquid generated low MN conversion, high DMO selectivity, while the catalyst synthesized under basic solution could increase MN conversion with slightly decreasing DMO selectivity. In view of the product's yield, basic precursor's solution is regarded to be more suitable for carbonylation catalyst's preparation (Table 1).

Hydrogenation process

Hydrogenation catalyst is the key during the whole technology to prepare MEG from CO and H_2. Current catalyst usually contains some chromium element, which is poisoning to the environment and people's life. Pujing developed a kind of green and high effective Cu/SiO_2 catalyst which performs very well during DMO hydrogenation reaction.

Table 2 illustrates that, our hydrogenation sample owns excellent activity for DMO and selectivity toward MEG. At low LHSV, the main by-product is BDO (1,2-butanediol) due to deep hydrogenation, with little MG (methyl glycolate) and PG (1,2-propylene glycol). Increasing LHSV up to 4.0 per h, the DMO conversion was still 99.0 %, with MG selectivity less than 2.0 %. When the LHSV went up to 8.0 per h, the conversion of DMO also reached 73.9 % more, with MG selectivity of 29.7 % and EG selectivity of 69.9 %. These results illustrated that the Cu–Si catalyst developed by Pujing Chemical has high potential for the hydrogenation process.

Except for the activity and selectivity during hydrogenation, the life time of the hydrogenation catalyst is another important factor, especially during industrialization. We verified our sample with results shown as follows. Figure 3 presents that after 4000 h's test, the catalyst still kept its high DMO conversion (almost 100 %) and high EG selectivity (>95.0 %).

Pilot plants

Laboratorial results just mean a possible scientific way to produce the objective products, however, in scaling-up process, heat transfer, mass transfer and momentum transfer usually play more important roles in industrial

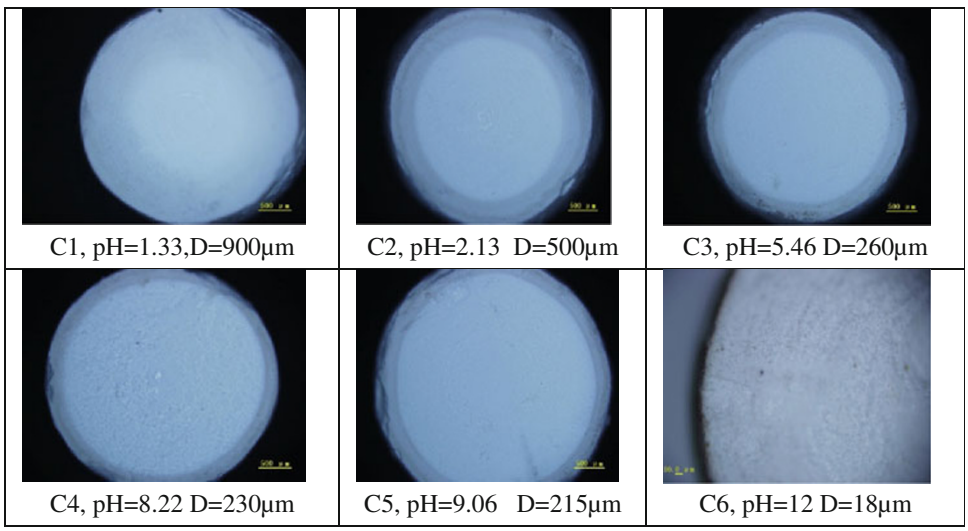

Fig. 2 The influence of pH value on the depth of egg shell for serial C catalysts

Table 1 Catalytic performance of serial C Pd/α-Al_2O_3

Catalysts	Precursor pH	Conversion of MN (%)	Selectivity (%)				Yield of DMO (%)
			DMO	DMC	ME	MF	
C1	1.33	75.34	93.96	4.02	1.87	0.15	70.79
C2	2.13	77.13	93.35	4.80	1.73	0.12	72.00
C3	5.46	83.01	91.32	6.50	2.05	0.13	75.80
C4	8.22	86.57	91.72	6.52	1.57	0.19	79.40
C5	9.06	87.68	91.71	7.14	1.02	0.13	80.41
C6	12.03	90.56	90.92	8.16	0.83	0.09	82.34

Table 2 The influence of LHSV on DMO conversion and productions distributions

LHSV (g/g h)	DMO conversion	MG selectivity	PG selectivity	MEG selectivity	BDO selectivity
0.7	100.00	0.39	0.01	95.28	3.16
1.0	99.99	0.11	0.00	98.26	1.46
2.0	99.97	0.34	0.00	98.70	0.86
3.0	99.87	0.90	0.00	98.31	0.71
4.0	99.55	1.57	0.00	97.36	0.93
8.0	73.98	29.72	0.00	69.94	0.33

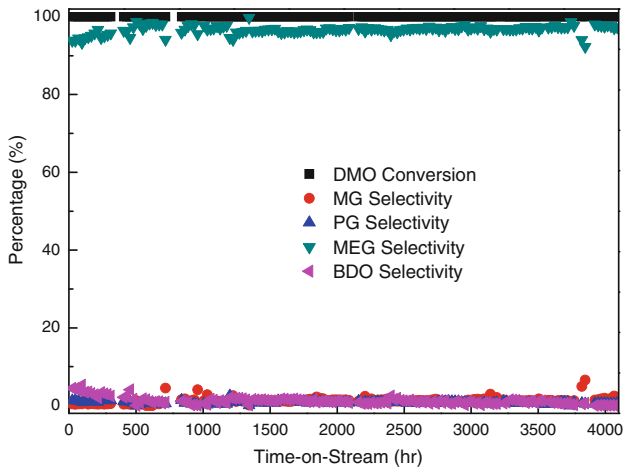

Fig. 3 The Steady Test of Pujing's Hydrogenation Catalyst 0.7 g/g h, 2.0 MPa, 195–215 °C H_2/DMO = 100:1 (mol:mol)

production process. To verify our industrial samples' activity and selectivity, we employed a 300 t/a pilot plant with starting material of DMO and H_2 and spent 1 week to perform hydrogenation reaction. The pilot plant consists of 30 tubes (Φ50 mm × 3.0 m for each tube), and the performance was shown in Fig. 4.

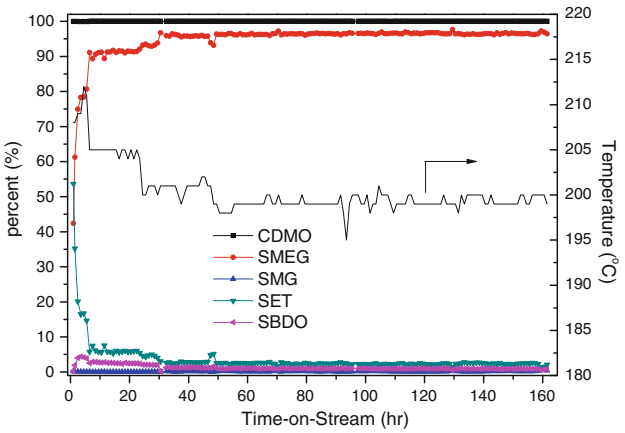

Fig. 4 300t/a Hydrogenation Pilot Plant LHSV = 0.7 h^{-1} g/g cat. P = 2.50–2.70 MPa, T = 200–205 °C, H_2/DMO = 66 (mol:mol)

The above results demonstrated that, the catalyst performed in excellence both in DMO conversion and in EG Selectivity. In the initial stage, deep hydrogenation occurred due to high catalytic bed temperature of 205 °C and consequently the byproducts of BDO and ET (ethanol) got high selectivity. After cooling down to 200 °C, DMO conversion kept high value of around 100 %and EG selectivity increased up to above 96.0 % at the expense of BDO and ET selectivity. Within 165 h' test, the sample stabilized its activity for DMO and selectivity toward MEG all the time.

The 300 t/a hydrogenation pilot plant gave a positive result for Pujng's sample, which incurred us to perform a whole verification on the schematic flow, reactor design, catalyst samples and the purification technology. Pujing spent over 65 million RMB to set up a 1,000 t/a pilot plant (Fig. 5) located in Anhui Province, China. In 2010, poly-ester grade EG product was obtained from the setup with MEG purity >99.8 % and UV transmittance >80 % (220 nm), with the starting materials of CO, O_2 and H_2.

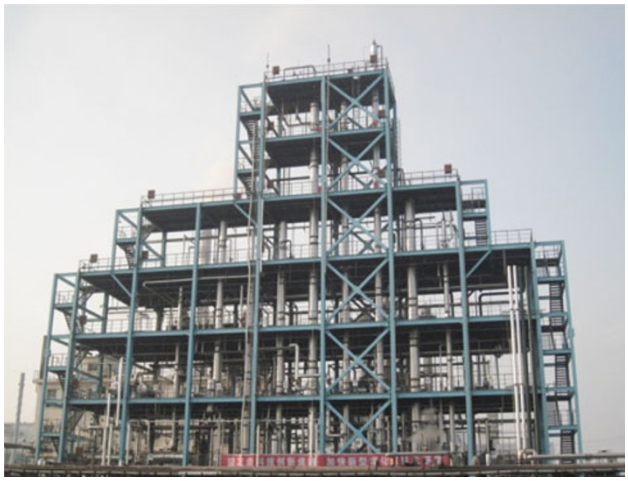

Fig. 5 1000 t/a MEG pilot plant in Anhui, China

Conclusions

The technology of syn gas to MEG is getting high attraction for those places that have ample CO and hydrogen, which could depress the import pressure of petroleum. The MEG technology developed by Pujing Chemical has passed step-by-step laboratory test and pilot plant's verification, and is going to industrialization. Up to now, one set of 300 kt/a MEG contract has become effective and the other sets are being under negotiation.

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